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Preliminary communication

SYNTHESIS OF PHOSPHA- AND DIPHOSPHA-ZIRCONOCENE DICHLORIDES

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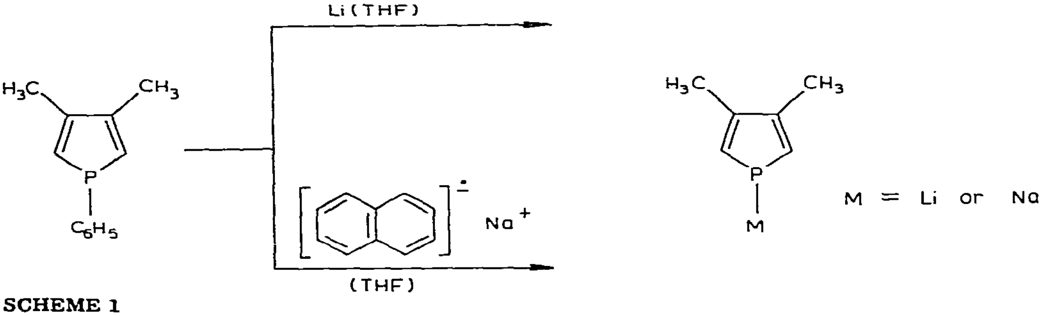
Summary

The reactions of η^5-$C_5H_5ZrCl_3$ or $ZrCl_4$ with a phospholyle anion lead to phospha- and diphospha-zirconocene dichlorides, respectively. These compounds, which are sensitive towards air, have been characterized by mass spectrometry and ^1H NMR spectroscopy.

There is increasing interest in organometallics involving heterocyclic ligands π-bonded to metals. This large number of organometallic compounds derived from borabenzene [1,2,3], pyrrole [4], phosphole [5—8], phosphorines [9] etc. have been recently described. For transition metals of Group IVB the only such compounds obtained involves the complexation of a pyrrole ring to zirconium [4]. However, the researches of Mathey [5,8] on phospha- and diphosphaferrocenes have shown that phospholyle ligands are more able to π-complexes with transition metals than pyrrolyl ligands. Therefore, it seemed of interest to examine the complexation of phospholyle ligands with Group IVB metals, and we describe below the initial results for the zirconium series.

As the starting compound we used the 1-phenyl-3,4-dimethylphosphole [10] and we first attempted to generate the phospholyl anion by use of lithium metal or sodium naphthalene, as in Scheme 1.



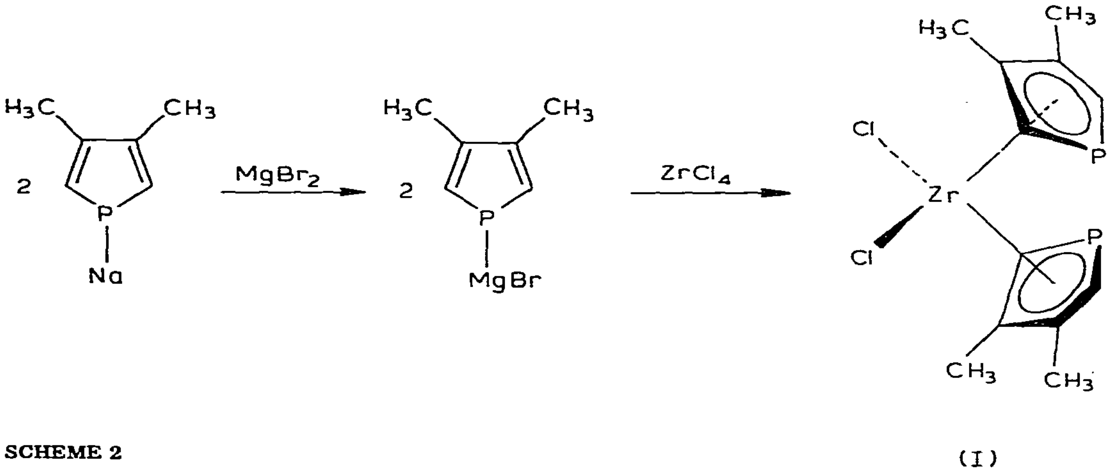
SCHEME 1

TABLE 1

MAIN IDENTIFIED FRAGMENTS (m/e) IN MASS SPECTROMETRY CONCERNING $LL'ZrCl_2$ ($L = \eta^5$-C_5H_5 or η^5-C_6H_8P) COMPOUNDS

$L = L' = \eta^5$-C_5H_5	M^+ (290)	$[M-Cl]^+$ (255)	$[M-C_5H_5]^+$ (225)		$[C_3H_3ZrCl_2]^+$ (199)	$[C_5H_5ZrCl]^+$ (190)	$[C_3H_3ZrCl]^+$ (164)	$[ZrCl_2]^+$ (160)	
$L = \eta^5$-C_5H_5, $L' = \eta^5$-C_6H_8P	M^+ (336)	$[M-HCl]^+$ (300)	$[M-C_5H_5]^+$ (271)	$[M-C_6H_8P]^+$ (225)	$[C_3H_3ZrCl_2]^+$ (199)	$[C_5H_5ZrCl]^+$ (190)	$[C_3H_3ZrCl]^+$ (164)	$[ZrCl_2]^+$ (160)	$[C_6H_8P]^+$ (111)
$L = L' = \eta^5C_6H_8P$	M^+ (382)	$[M-HCl]^+$ (346)		$[M-C_6H_8P]^+$ (271)				$[ZrCl_2]^+$ (160)	$[C_6H_8P]^+$ (111)

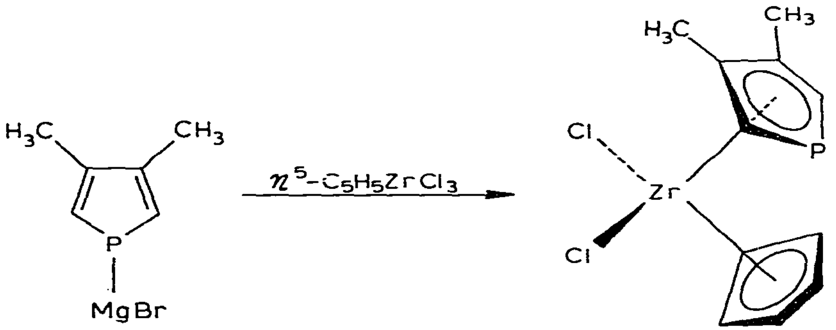
In both cases, action of $ZrCl_4$ on the anions we obtained led to a complex mixture in which no definite compound could be identified. We then tried the technique described by Mathey [8], and first treated 1-phospholylsodium with anhydrous magnesium bromide. The resulting organomagnesium compound was treated with $ZrCl_4$ to give diphosphazirconocene dichloride (I) in about 30% yield (Scheme 2).



SCHEME 2

Complex I is a solid, sensitive towards air and almost insoluble in the common solvents.

The action of η^5-$C_5H_5ZrCl_3$ on the phospholyle anion similarly gives phosphazirconocene dichloride (II) (Scheme 3).



SCHEME 3

(II)

The compounds I and II show very similar stabilities and solubilities. The novel complexes we have obtained were characterized by their mass and ^1H NMR spectra.

The main features of the mass spectra are listed in Table 1, in which data for $(\eta^5$-$C_5H_5)_2ZrCl_2$ [11] were included for comparison.

The following features are of interest:

(a) As for the zirconocene dichloride, the molecular peaks are very intensily in compounds I and II, which means that the three molecules show similar

TABLE 2

^{1}H NMR CHARACTERISTICS^a (100 MHz) CONCERNING LL′ZrCl$_2$ COMPOUNDS

	Methylic protons (δ (ppm))	Cyclopentadienic protons (δ (ppm))	Phospholic protons (δ (ppm))
L = L′ = η^5-C$_5$H$_5$ [12]		s 6.50^b	
L = η^5-C$_5$H$_5$, L′ = η^5-C$_6$H$_8$P	s 1.98	m 6.03	d 6.29 and 6.65 (J(HP) 36.5 Hz)
L = L′ = η^5-C$_6$H$_8$P	s 1.99		d 6.54 and 6.92 (J(HP) 37.6 Hz)

^{a}s, singlet; d, doublet; m, multiplet. ^{b}60 MHz (CDCl$_3$).

stabilities towards the electronic bombardment.

(b) The fragmentation modes of the three compounds are much the same. In the spectra, identical or similar fragments are effectively observed, in particular $ZrCl_2^+$, $[M-C_5H_5]^+$ or $[M-C_6H_8P]^+$, $C_3H_3ZrCl^+$ $[C_5H_5ZrCl]^+$.

(c) For compound II, both $[M-C_5H_5]^+$ and $[M-C_6H_8P]^+$ fragments are present, indicating comparable stabilities for these two types of π-bonds.

The similarity of the behaviour of these three compounds indicates unambiguously the structures of complexes I and II.

In spite of their low weak solubilities, we were able to obtain ^{1}H NMR spectra (C_6D_6). The results are shown in Table 2, and fully confirm the structures proposed.

Synthesis of analogous complexes derived from hafnium and of those bearing non-substituted phospholyle ligands and a study of their reactivities is in progress.

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